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A C^{14} dating station using the CO_2 proportional counting method

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With 11 figures in the text

Introduction

A. *Principles and occurrence in nature of* C^{14}

Among the natural radioactive isotopes the C^{14} isotope is suitable for the determination of ages up to about 50000 years.

C^{14} is produced in the atmosphere by thermal neutrons and nitrogen at an altitude of about 16000 m, where the neutron density has a maximum, according

$$N^{14} + n \rightarrow p + C^{14}. \tag{1}$$

Other possible reactions for nitrogen are

$$N^{14} + n \rightarrow C^{12} + H^3, \tag{2}$$

$$N^{14} + n \rightarrow 3\,He^4 + H^3, \tag{3}$$

$$N^{14} + n \rightarrow B^{11} + He^4. \tag{4}$$

However, the dominant reaction is the first one [1]. The cross-section for thermal neutrons and O^{16} is only about 1 ‰ of that for N^{14}.

The C^{14} isotope is β-active:

$$C^{14} \rightarrow N^{14} + \beta^- \tag{5}$$

with a half-life of 5568 ± 30 years [2, 3, 4] and a maximum energy of about 157 keV [5]. The half-life measurements are made with a mixture of CO_2 and argon-alcohol or CO_2 and methane in proportional counters. Recent measurements, however, have given for instance 5900 ± 250 [6] and 5370 ± 200 [7] years, which indicates that the limits are too narrow.

The C^{14} isotopes react with oxygen to give carbon dioxide and all living things as well as the inorganic carbon in the oceans and subsoil water will be radioactive.

In 1946 Libby [8] estimated that one gram of carbon should give a few decays per minute and the following year he published the first measurements which confirmed that the C^{14} isotope could be used for age determinations of organic materials [9].

In performing the measurements one makes use of the common disintegration law

$$N = N_0 e^{-\lambda T}, \tag{6}$$

where N_0 is the acitivity at the time when the exchange of carbon dioxide with the surroundings ceased (e.g. by the death of an organism, by the completion of a tree ring), N is the activity after the time T and λ is the disintegration constant.

Datings with C^{14} are based on the assumption that the specific activity of carbon has been constant in the exchange reservoir over the whole world during a period longer than the intervals to be determined. The amount of carbon in the CO_2 reservoir has been given by Anderson [10].

	gm C/cm² of the surface of the earth
Ocean, dissolved inorganic mat.	7.25
Ocean, dissolved organic mat.	0.59
Biosphere	0.33
Atmosphere	0.12
Total	8.3

The amount of water in the oceans was lower by some per cent during the last Ice Age while the temperature was also slightly lower and these two facts might have raised the specific activity [1]. Since fossil coal and oil have been burnt in very large quantities during the last years the amount of inactive carbon might have increased relative to radio-carbon. This is the reason why, as standards, one often uses samples about 100 years old. Sometimes natural isotope fractionation occurs e.g. for animals living in the sea. One has discussed if one can apply a general correction for shells, but the best procedure is to measure the C^{13}/C^{12} fraction and then to apply a correction. The C^{13} and C^{12} isotopes are not radioactive. One can expect that the enrichment of C^{14} is twice that of C^{13}.

Comparison with historically known samples [1] shows that C^{14} datings are reliable up to about 5000 years from now, whereas comparison with samples determined by the ionium method indicates [11] that the C^{14} datings are reliable up to about 30000 years. Ionium-determined ages are sensitive to the original ionium concentration in the sediments and climate differences can change the deposits [12]. Because of this the comparison with the ionium method has been questioned. The C^{14} dates are at least comparable within a C^{14} timescale.

B. *Different methods for C^{14} dating*

Since the C^{14} concentration is very small, 10^{12} C^{12} atoms per C^{14} atom, the intensity will be about 13 c/min and gm for modern carbon. To measure such a low activity one has to reduce the background as much as possible. One has used methods with solid carbon inside Geiger counters, with gaseous samples in Geiger counters and proportional counters and with scintillation counters.

Tables 1–3 show a comparison between different stations.

I. GAS-FILLED COUNTERS

(*a*) *Methods*

1. *Solid carbon* (*Libby's method*)

Libby [1] used a Geiger counter with solid carbon on the inside. The method has been developed e.g. in Copenhagen [13, 14] where one has employed a counter with three tubes lying in a row. The central tube was used for unknown samples and the other two for background measurements. In Rome [15] a counter with four elements is used. When using the solid carbon method one first combusts the sample to carbon dioxide and then reduces the gas with magnesium. As the solid carbon can easily absorb radioactive gases and dust from atomic weapons tests the risks for contamination have been so great that it has been almost impossible to make determinations with the solid carbon method. Other objections are that the chemical treatment takes rather long time and that fairly large quantities of carbon are needed, partly due to the fact that the sample is deposited on the counter wall (lowering the efficiency by 50%) and partly due to the self-absorption. The total efficiency is only about 5%. One usually choses a layer thick enough to absorb the radiation from the innermost parts to more than 99.0 % to avoid errors due to variations in the thickness of the sample. The range for β-rays from C^{14} is only 28 mg/cm^2. It is also very important that the chemicals used are pure and one always has to examine the samples on their ash content.

2. *Cases when the sample is converted to a gas*

(α) Geiger counters filled with CO_2–CS_2 mixtures have been used by Crane [16] and Moscicki [17], but the sensitivity of these systems is very low.

(β) Douglas [18] has used ionization chambers.

(γ) Proportional counters filled to a pressure above one atmosphere give good results due to the 4π geometry and the fact that the background increases very slowly with pressure.

De Vries and Barendsen [19, 20, 21, 22] have shown that carbon dioxide is a good counting gas but has to be sufficiently free from electro-negative impurities—of oxygene one can tolerate about 1×10^{-3} mm partial pressure in three atmospheres.

Burke and Meinschein [23, 24] have used methane and they think that it has the advantage over carbon dioxide that it is much less sensitive to electronegative impurities. The operating potential is lower than that for carbon dioxide.

A gas containing two carbon atoms per molecule will give twice the counting rate for the same volume, pressure and temperature compared to carbon dioxide and methane. Faltings [25] has used ethane and Loosemore [26], Suess [27, 28] and others have used acetylene. Acetylene, however, cannot be used at higher pressure due to the risk for explosions.

Carbon dioxide is either produced according to the "dry" method, which has been adopted in Uppsala, or the "wet" method. In the first case a CaO-oven is usually employed for absorbing the carbon dioxide when radioactive purification is desired. The gas can also be purified from gases other than radon with the CaO furnace, but often difficulties in the absorption will arise, if the gas is not pure. De Vries [29] has developed a new system for radioactive purification. The gas is carefully condensated and some carbon dioxide with enriched radon can be pumped off. In the "wet" method the carbon dioxide is trapped in ammonia after which it is precipitated with calcium chloride and liberated with acid.

Methane can be produced in the following way. The sample is combusted to carbon dioxide and reduced with magnesium to elementary carbon, which is washed and filtered several times. Aluminium and carbon form carbide at 1200°C in helium and then methane is liberated with water. Methane can also be produced from carbon

Table 1. Comparison between different stations using solid carbon.

Investigator . . . . . Reference	Libby [1]	Kulp [30]	Anderson Levi Tauber [14]	Crane [45]	Ballario [15]
Shield	20 cm Fe	20 cm Fe 2.5 cm Hg	20 cm Fe	20 cm Fe	> 20 cm Fe
Recent carbon S_0 c/min .	6.7	6.7	5.9	8	5.4
Background B c/min . .	5	2	5.8	8.4	15.5
Max. age 4 σ criterion 48 hours	29 000	33 000	28 000	29 000	23 000
Factor of merit $S_0/\sqrt{B}$.	3	4.7	2.5	2.8	1.4

dioxide and hydrogen at 475°C with ruthenium as a catalyst. The synthesis according to this method will take one hour (the time for catalyst preparation not included).

Acetylene and other counting gases are also produced from carbon dioxide.

(*b*) *Shielding*

Common for the above-mentioned methods is the necessity of a heavy shield.

Libby originally used only iron (γ-absorbent) and a set of Geiger counters in anticoincidence with the main Geiger counter (eliminating the mesons in the cosmic radiation). Kulp [30] introduced a mercury layer between the main counter and the a.c. counters and reduced the background in that way. He got the best result by using doubly distilled mercury. 1″ of mercury reduced the background from 3.8 c/min to 2.2 c/min. The mercury will absorb γ-radiation from the iron. De Vries and Barendsen [21] obtained the same result with carefully chosen lead as with mercury. Kulp at the same time reported that he lowered the background with another 0.1 c/min by using additional a.c. counters at the end of the ordinary a.c. ring, but de Vries [31] got no improvement with a set of counters in front of the proportional counter. De Vries [31, 32] has proved that part of the background is due to the soft component of the cosmic radiation which produces neutrons in the iron shield. He has further proved that one can reduce the background appreciably by placing blocks of paraffin, mixed with boric acid, inside the shield. At the same time the variations with barometric pressure will be less. He has also proved that a hydrogen-containing gas (propane) will give a higher background even if all other conditions are the same. In propane mainly the recoils of fast neutrons are detected, whereas in carbon dioxide mainly the γ-rays, produced by the capture of slow neutrons, are counted.

(*c*) *Counters of special design*

In Bern [33] one has made a counter with the a.c. counters built into the same tube as the main counter, so that the same gas is used in the whole system. The inner counter as well as the outer counters work in the proportional region. A polystyrene foil with aluminium on both sides limits the inner counter.

In Trondheim [34] a counter is used with a screen and the high voltage is put on this screen which thus constitutes the wall of the counter.

Table 2a. Comparison between stations using gaseous samples.

Investigator Reference	Moscicki [17]	de Vries [21, 31]				Fergusson [38]		Brannon [46]	Tauber Private comm.	Nydal [34]	Olsson
Type of counter	Geiger	Prop.	Prop.	Prop.		Prop.		Prop.	Prop.	Prop. Spec. design	Prop.
Gas	CO_2+CS_2	CO_2	CO_2	CO_2	C_3H_8	CO_2		CO_2	CO_2	CO_2	CO_2
Shield	15 cm Pb	60 cm Fe + + 15 cm paraffin and boric acid + 10 cm Fe				20 cm Fe		10 cm Fe	20 cm Fe	Bomb shelter + 20 cm Fe	40 cm Fe + + 15 cm paraffin and boric acid + + 10 cm Fe
		3.2 cm Pb				2.5 cm Hg		2.5 cm Hg	2.5 cm Hg		3 cm Hg
Total volume										6.2 lit.	
Sensitive vol.	0.3 lit.	0.3 lit.	0.7 lit.	2 lit.		6 lit.		0.7 lit.	2 lit.	2.5 lit.	0.45 lit.
Pressure	0.5 atm.	3 atm.	3 atm.	3 atm.	2 atm.	3 atm.	1 atm.	10 atm.	2 atm.	4 atm.	3 atm.
Recent carbon S_0 c/min	1.7	5.64	14.6	37		103	37.5	45.2	24.8	58	9.0
Background B c/min	11	2.4	0.92^a	2.44^a	4.00^a	14	9.8	13.5	5.3	14.9	0.98^b
Max. age 4σ criterion 48 h	16 000	31 000	42 000	47 000		47 000	41 000	41 000	40 000	43 000	38 000
Factor of merit $S_0/\sqrt{B}$	0.51	3.6	15.2	24		28	12.0	12.3	11	15	9.2

[a] At 766 mm Hg. [b] At 755 mm Hg. (Compare note on p. 44).

Table 2b. Comparison between stations using gaseous samples.

Investigator . . .	Burke	Diethorn	Crathorn Loosemore	Suess	Preston	Oeschger	Faltings	Curra
Reference	[24]	[47]	[26]	[27, 28]	[48]	[33]	[25]	[35, 36,
Type of counter .	Prop.	Prop.	Prop.	Prop.	Prop.	Prop. Spec. design	Prop.	Prop. Spec. design
Gas	CH_4	CH_4	C_2H_2	C_2H_2	C_2H_2	C_2H_2	C_2H_6	
Shield	20 cm Fe 2.5 cm Hg	35 cm Fe 2.5 cm Hg	27 cm Fe	21 cm Fe 1.5 cm Hg	20 cm Fe 1.25 cm Hg			
Total volume . .		1.9 lit.			2.5 lit.			
Sensitive volume						1.5 lit[a]		5.5 lit.
Pressure	2 atm.	5 atm.	126 cm		68 cm	71 cm	2.7 atm.	1 atm.
Recent carbon S_0 c/min	7.5	30.7	39	15.8	28.4	15.5	20	
Background B c/min	2.6	13.6	16	2.3	8.2	0.95	98	2.2
Max. age 4σ criterion 48 h . . .	33 000	38 000	39 000	40 000	39 000	43 000	26 000	
Factor of merit $S_0/\sqrt{B}$	4.7	8.3	9.8	10	9.9	15.9	2.0	

[a] Dead volume = 0.9 l (at the sensitive part of the wire) plus the parts at the ends.

Curran [35, 36, 37] already earlier proposed a system with a screen and built-in a.c. counters. Curran reduced the background further by putting the whole counter into a magnetic field directed along the axis of the counter.

The advantage of these counters is that the wall effect due to the capability of the γ-rays to produce photo- and Compton electrons decreases. The method is especially applicable when the samples are large, but this is not always the case with C^{14} samples.

(*d*) *Electronic systems*

When recording β-rays from C^{14} one can use rather slow systems. Usually the counting rates with and without a.c. counters are recorded. De Vries and Barendsen [21] have used a system with 4 channels (β, α and 2 channels for mesons) all with discrimination for low energy particles. Fergusson [38] has used a four-channel height- and coincidence analyzer. We use the system described by Barendsen.

(*e*) *Effect of isotope enrichment*

It is possible to extend the limit of age by applying isotope enrichment. This would be of value when large samples of great importance are determined.

II. SCINTILLATION COUNTERS

Although scintillation counters are not common for routine dating they give results quite comparable with those from the proportional counters. The problems in connection with scintillation counters are not the same as for proportional counters.

Table 3. Comparison between stations using scintillation counters.

Investigator	Arnold		Audric	Pringle			Barendsen
Reference	[39]		[42]	[43]		[44]	[49]
Substance	Ethanol	Aliphatic hydrocarbon	Acetylene in toluene	Toluene	Methanol	Trimethylborate	Liquid CO_2 in toluene
Shield	Hg	Hg	Fe	12.5 cm Pb 3.8 cm Hg			12.5 cm Fe 1.25 cm Pb
Recent carbon S_0 c/min	54	182	90	15.5	14.2	10	9.1
Background B c/min	26	26	100	3.3	6.2	4.3	15.5
Max. age 4σ criterion 48 h	40 000	49 000	38 000	38 000	35 000	33 000	28 000
Factor of merit $S_0/\sqrt{B}$	11	36	11	8.5	5.7	4.8	2.3

One uses liquid scintillators. The volume is small and one does not need heavy iron shields. The background is mainly determined by the dark current of the photo multiplier and it may be very high for the energies involved in C^{14} dating. Therefore, it is advisable to use channel discrimination. One can also use cooled photo multipliers and have two photo multipliers in coincidence. The height of the pulses can be regulated with a stream of oxygen or nitrogen through the scintillator. Arnold [39], Audric and Long [40, 41, 42] and Pringle *et al.* [43, 44] have used different substances. One has to convert the sample into a compound that can be dissolved in the scintillator or a substance which can dissolve the scintillator.

What is common for the different methods is the fact that the synthesis is rather elaborate and, in addition, that the risk for isotope fractionation is greater. One has to check this carefully as the yield is less than 100 %. However, Barendsen [49] has used liquid carbon dioxide as diluent and his method has not these disadvantages.

Description of the Uppsala station

A. *The proportional counter*

The counter was designed in collaboration with professor de Vries. Calculations and experiments made by de Vries *et al.* in Groningen were kept in mind during the construction to get small end effects and a small dead volume in the counter itself. The material in the counter was chosen in view of the good reults that were obtained with the first quartz counter in Groningen. In this case the counter was designed to stand a high pressure. Part of the counter used in Uppsala was manufactured in Groningen. Professor de Vries is completing a counter of the same design. A detailed description of the counter will be published later. Here a very short description will be given.

The counter consists of a quartz tube inside a copper tube. The quartz also serves as an isolator. Both sides of the tube are made conducting with a layer of tin oxide. The inner side serves as the cathode. The high-voltage is put entirely on the cathode. The counter can be taken apart because of two teflon rings. All solderings are made of pure tin or silver. Quartz to metal seals are made with araldite polymerized at about 190°C.

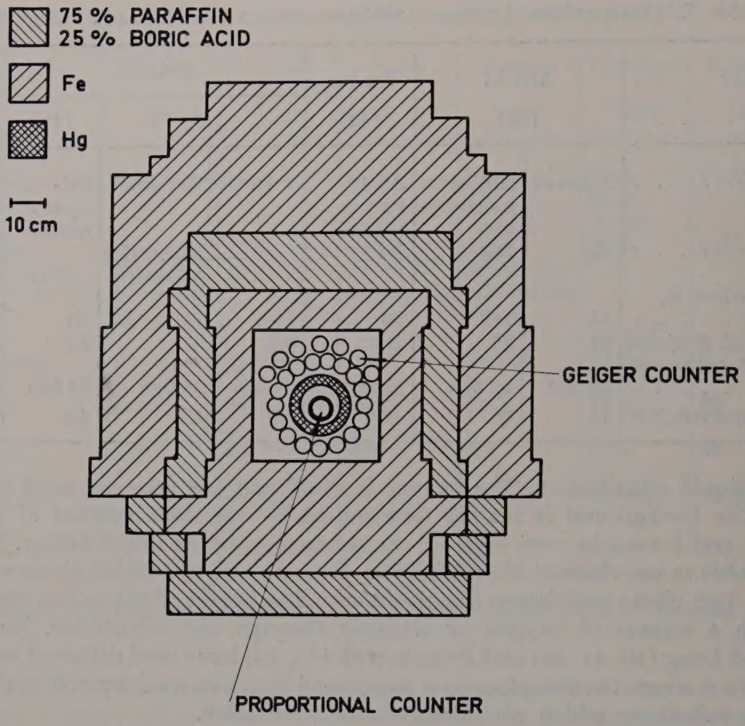

Fig. 1. A vertical section of the whole shield perpendicular to the axis of the proportional counter.

Wire: Stainless steel, 0.05 mm ∅
Sensitive length, 300 mm
Inner diameter of the counter: 45 mm
Background 0.98 c/min at 20°C and 3 atm CO_2 (bar. pressure 755 mm)[1]
Modern carbon 9.0 c/min at 20°C and 3 atm CO_2
Maximum age 38 000 years at 3 atm CO_2 with the usual criterion of net counting rate = 4 σ, where σ is the statistical deviation at 48 hours of counting.

B. *Shielding*

The counter has not yet been tested without a shield but the background in that case is estimated to be about 380 c/min.[2] Fig. 1 shows the shield that surrounds the proportional counter. The whole shield is covered with a plastic cloth to prevent dust from penetrating between the iron blocks. Fig. 2 shows the counters and the mercury vessel inside the shield. When the station is operating, the proportional counter is actually placed further inside the hole. A photograph of the whole shield and the electronics is shown in Fig. 3 (the plastic cover was removed when the photograph was taken). A detailed description of the shield will be given below.

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[1] *Note added in proof.* — The background was reduced to 0.96 c/min (bar. pressure 745 mm) after we had adjusted the electronics.

[2] *Note added in proof.* — The background proved to be about 680 c/min when the counter was about 70 cm in front of the shield (thus partly shielded).

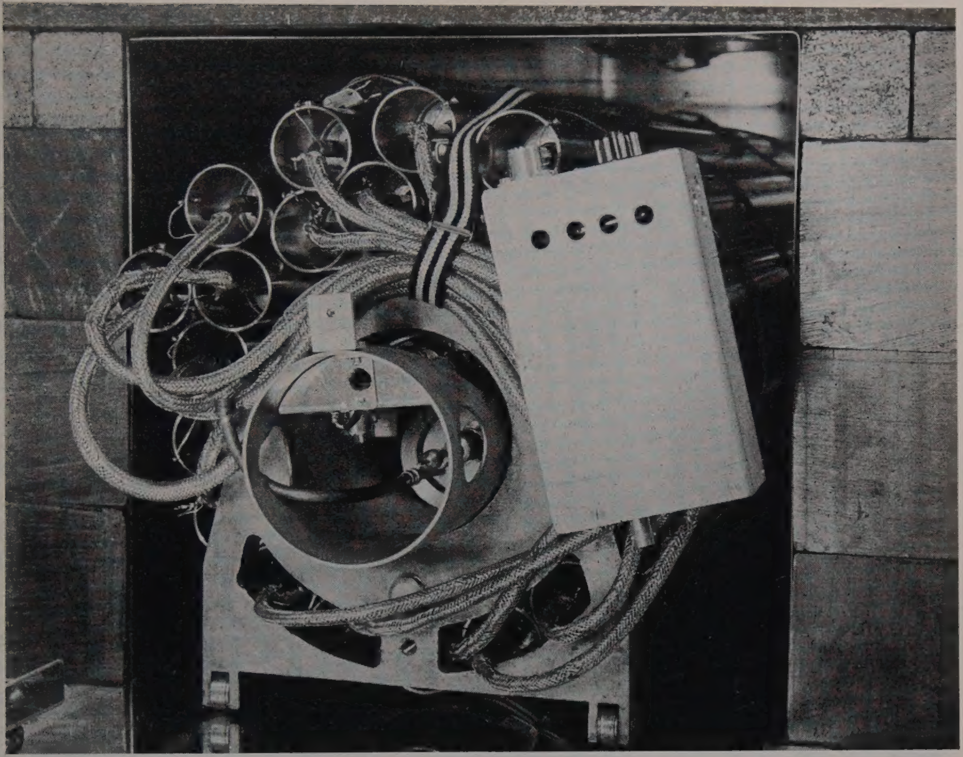

Fig. 2. The mercury tank with the proportional counter and the Geiger counters. The position of the proportional counter is only temporary—in reality the counter lies further back. The box contains the preamplifier of the Geiger counters.

I. *γ-radiation from outside*

190 c/min are probably due to gamma-radiation from outside. The first 10 cm layer of iron will reduce this contribution to the background to 5 to 10 c/min. The next layer will reduce it to about 0.5 c/min and the third layer to about 0.05 c/min [21].

II. *γ-radiation from the iron shield*

Usually the iron itself is slightly radioactive and the background can be reduced with a layer of mercury. In this case a layer, 3 cm thick, has been used between the proportional counter and the Geiger counters. The mercury has been doubly distilled. No measurements have been made here of the effect of this mercury but comparison with results at other laboratories indicates a reduction of 1 to 10 c/min. The mercury is contained in the cavity between the walls of two concentric cylinders. The effective length of the vessel is 750 mm. The inner diameter is 100 mm.

III. *The hard component of the cosmic radiation*

The intensity of the mesons is not reduced very much with the iron but the mesons can be detected very efficiently with Geiger counters. We have 17 Geiger counters

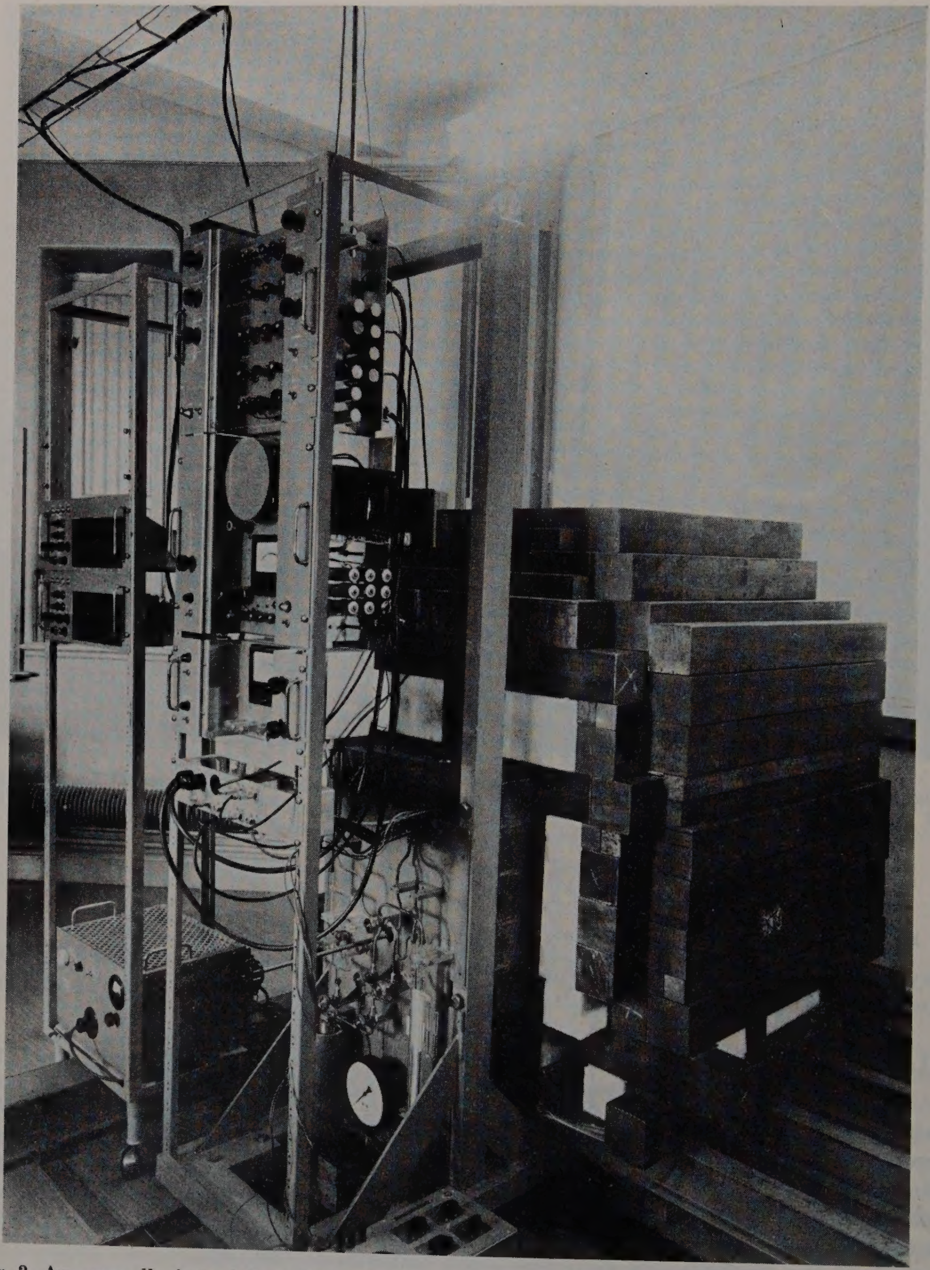

Fig. 3. An over-all view of the shield and the electronics. The filling system and the front wall of the shield are attached to the right rack which can be drawn out on rails. The mercury tank can be left inside the shield or drawn out together with the front wall. The proportional counter is also connected to the rack. The whole iron shield rests on rails. To the right of the racks there is a Wheatstone bridge for measuring the temperature of the counter with a resistance thermometer.

Table 4. The lowering of the background due to the second layer of Geiger counters.

		Number of extra Geiger counters			
		1	3	5	7
Lowering of background c/min	1.5 mm wall	0.25 ± 0.06	0.40 ± 0.05	0.48 ± 0.05	0.51 ± 0.04

arranged in a circle around the mercury vessel. The counters have a wall thickness of 1.5 mm and for that reason we have put another set of counters (seven) above the others to detect the mesons that would otherwise have gone through the walls.

Table 4 gives the efficiency of the "extra Geiger counters".

The Geiger counters have a sensitive length of 630 mm, an inner diameter of 39 mm, an outer diameter of 42 mm, and a wire of tungsten 0.1 mm ∅.

The common plateau is about 100 volts with a slope of 8 %/100 volts.

IV. *The soft component of the cosmic radiation*

The neutrons produced in the outer parts of the iron shield are slowed down and captured in paraffin blocks (75 % by weight of paraffin and 25 % by weight of boric acid). There are 10 cm of iron between the counter and the paraffin which lies above and along the sides of the counter. For technical reasons we have put the paraffin that lies behind and beneath the counter outside the iron. The background has probably been lowered with about 0.6 c/min with this arrangement but still about 0.2 will be left due to the soft component [31].

C. *Electronics*

I. *Amplifiers and discriminators*

A block diagram over the electronics is shown in Fig. 4. The pulses from the proportional counter are fed to a cathode follower located next to the proportional counter inside the iron shield. From the cathode follower the pulses are fed to amplifiers, discriminators, pulse shapers etc. The pulses from the Geiger counters are fed to a pre-amplifier also located inside the iron shield and from there they are fed to an amplifier, a discriminator etc. The amplifiers consist of pentodes, the discriminators of Schmitt triggers and the pulse shapers of univibrators. The anticoincidence traps are hexodes. The pulses from the proportional counter are shaped to square pulses with a length of $80\,\mu s$.

Channel 1.—Here the sum of the meson component, the background and the C^{14}-electrons are counted. From the univibrator the pulses are fed to the scaler via a cathode-follower.

Channel 2.—All pulses from channel 1 are fed to the a.c. trap. The background and the C^{14} pulses are fed via a cathode-follower to the scaler.

Channel 3.—The pulses from the first amplifier in channels 1 and 2 are attenuated and fed to the discriminator. The threshold is adjusted so that the channel registers the most energetic half of the mesons, i.e. the threshold corresponds to an operating

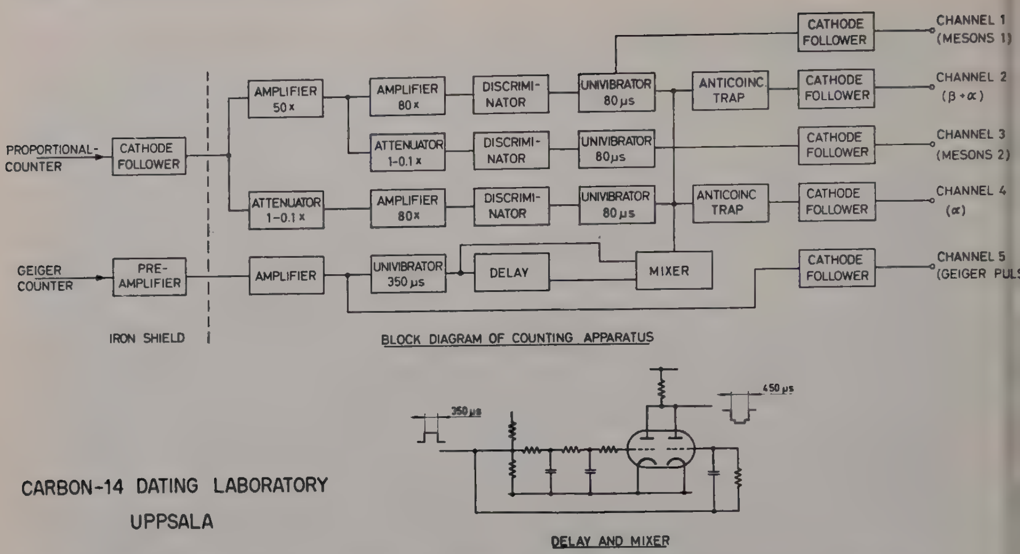

Fig. 4. Block diagram of the electronic system. (Channel 1 and 3 count in fact mesons + β- and α-particles.)

potential of 6500 volts for channel 1 (Fig. 5) although the potential of the counter is 7600 volts.

Channel 4.—The pulses from the common cathode-follower are amplified and the threshold is adjusted so that the channel counts pulses corresponding to what should be counted by channel 2 if the counter was operated at a potential of 5900 volts. As there is an a.c. trap this channel is sensitive to α-particles.

Channel 5.—The pulses from the Geiger counters are shaped to square pulses with a length of 350 μs. From the univibrator the pulses are fed to a mixer both directly and via a delay (Fig. 4). The pulses are fed to the grids and are taken from the common anode of a double triode. In this way we get a pulse blocking the anticoincidence trap for 450 μs although the other parts of the electronics are blocked only for 350 μs. A cosmic particle arriving during the last 80 μs of these 350 μs, when the anticoincidence trap is blocked by the preceding cosmic particle, and giving rise to a pulse in the proportional counter, will thus not give any ouput pulse from channel 2, as the mixer in channel 5 has then lengthened the anticoincidence-pulse to cover this second cosmic particle. The background is thus reduced with N c/min

$$N = N_{\text{Prop}} \cdot N_{\text{G}} \cdot T_{\text{Prop}}. \tag{7}$$

N_{Prop} and N_{G} are the number of cosmic particles detected in the proportional counter and the Geiger counters respectively, T_{Prop} is the length of the pulse from the proportional counter when it is fed to the anticoincidence trap. In this case we get

$$N = 100 \cdot 1800 \cdot 80 \cdot 10^{-6} \cdot 1/60 \text{ c/min} = 0.24 \text{ c/min}.$$

In the α- and β-channels the pulses are also delayed so as not to arrive before the pulses from the Geiger counters.

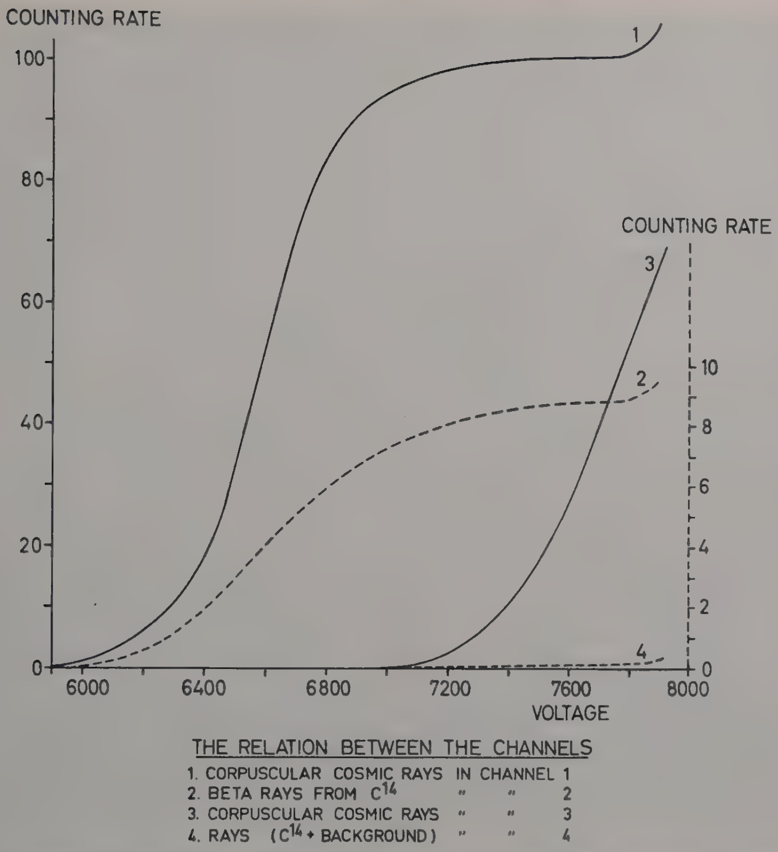

Fig. 5. The counting-rates in the different channels. All rates are expressed in counts/min. (Channel 4 counts mainly α-particles.)

II. *High voltage supply*

The high voltage supply has been designed by Ing. B. Johanssson [50]. It gives a negative voltage with a stabilizing factor of 100. The upper limit is 20 kV.

III. *Stabilizing*

All the electronic apparatus are fed with alternating current from a tube-controlled stabilizer. We are going to introduce a filter to suppress any disturbing signals transmitted through the main supply.

D. *Combustion and purification of the samples*

I. *Pre-treatment*

Foreign materials like roots in wood and charcoal are first removed. Organic samples are boiled with diluted acid so that the carbon in the carbonate is driven out as carbon dioxide.

Humic acid can be extracted with sodium hydroxide when necessary. The samples are slightly acid before they are dried after the pre-treatment to prevent carbon dioxide in the air from being absorbed.

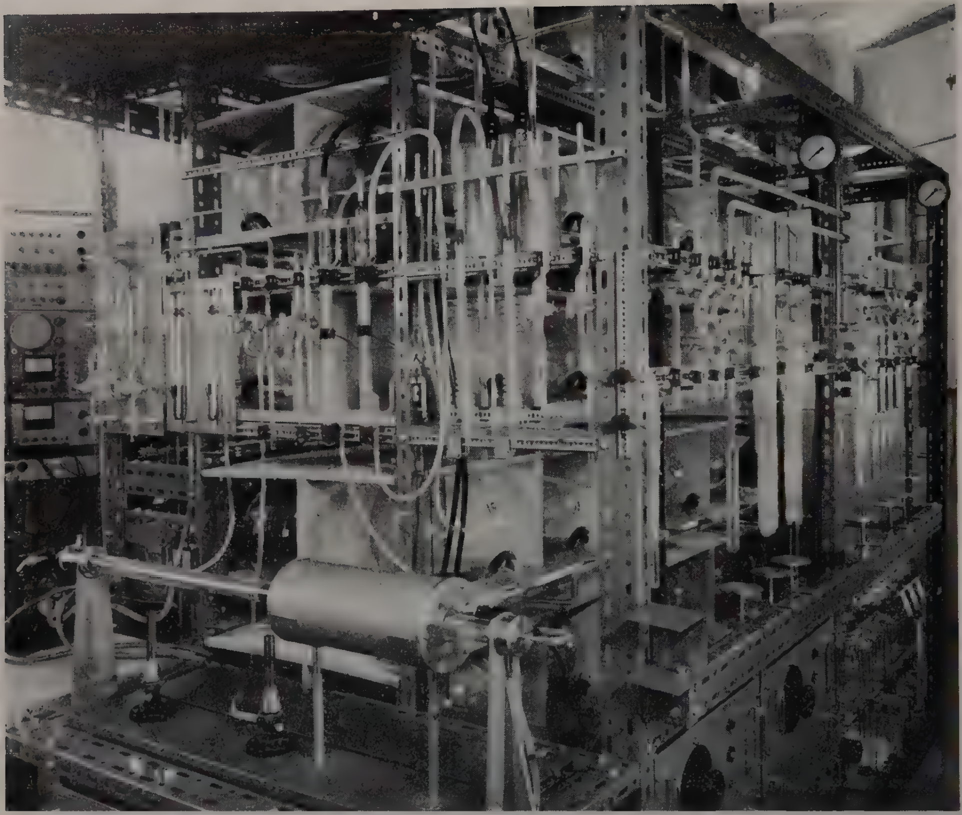

Fig. 6. An over-all view of the chemical apparatus. The two sides of the rack shown in the figure correspond to the chemical line from the combustion furnace to and including the three containers for samples that have not yet been completely purified. The part shown at the lower right is a filling system for Geiger counters.

II. *Combustion and purification of the gas*

Fig. 6 and 7 show two photographs of the chemical apparatus. Fig. 8 gives a schematic diagram of the chemical line.

(*a*) If the sample consists of a carbonate the carbon dioxide is driven out in a special piece of apparatus (shown to the left in the foreground of Fig. 6 and 7) and then it passes the same way as the ordinary samples.

(*b*) Organic samples are combusted in a quartz furnace (Fig. 8). The sample is put into the inner tube which ends in a small opening, 1 mm ∅, in front of some platinized asbestos. The sample is first outgassed in a weak stream of oxygen while a stronger stream passes in the outer tube. The oxygen goes from the bomb through a washing bottle with sodium hydroxide where carbon dioxide is absorbed. The sample and the catalyst are heated with Bunsen burners. The expelled gases are burnt at the small opening, the flame being initiated by the catalyst. During the combustion the stream of oxygen in the inner tube is stronger.

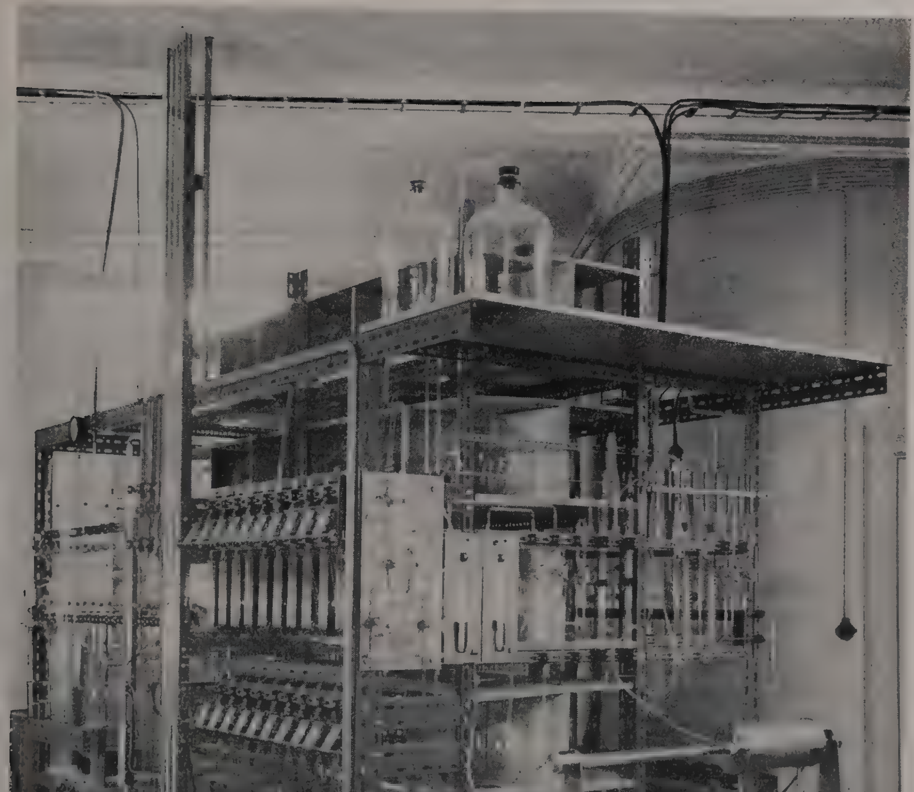

Fig. 7. An over-all view of the chemical apparatus. To the left is shown the purifying system from the copper furnace to the storing bottles.

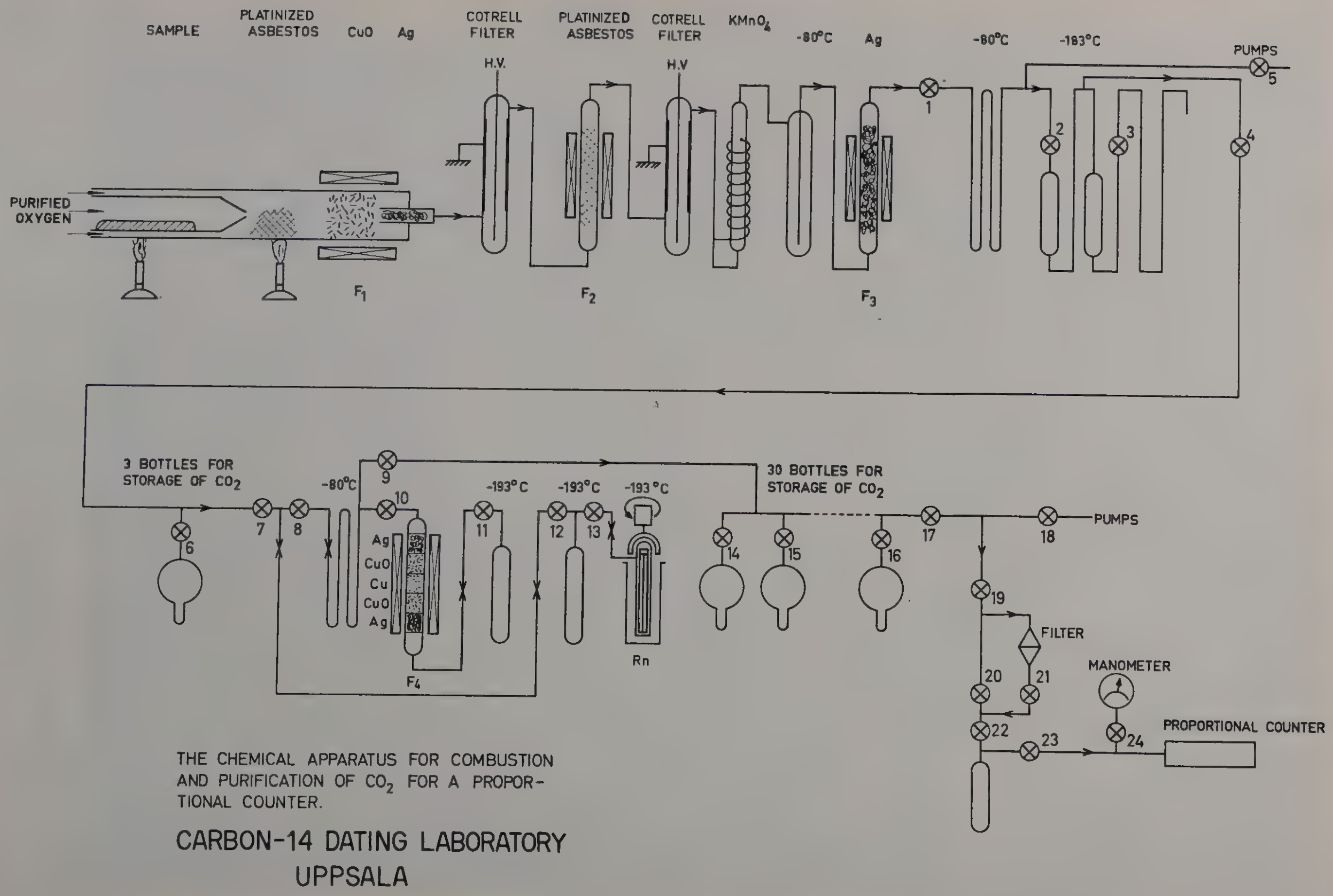

Fig. 8. A diagram of the chemical apparatus. A furnace with lead chromate will also be used.

The first furnace (F_1) contains copper oxide, which is a reserve for oxygen, and silver, which is replaced for every sample. Halogenes and sulfur trioxide are bound by the silver. From the first furnace the gases go to a Cotrell filter to be freed from dust and vapours. The next step is a furnace with platinized asbestos which catalyzes the reaction of sulfur dioxide and oxygen going to sulfur trioxide after which the gases are led through another Cotrell filter and two spiral bottles with potassium permanganate solution which oxidizes any remaining sulfur dioxide to sulfur trioxide. Most of the water vapour is trapped in the first trap, cooled with a mixture of acetone and carbon dioxide before the gas goes to the third furnace (F_3) which contains silver. The gas passes another trap kept at -80°C and is then frozen out with liquid oxygen in the trap between stopcocks 2 and 3. If, during the combustion, one wants to avoid pumping or if one wants to avoid the extra work involved in separating large amounts of oxygen from the condensed carbon dioxide one has to use a temperature in the trap that is not lower than that of liquid oxygen. During the combustion the stopcocks 1, 2 and 3 are kept open in order to let the oxygen escape into the air. After pumping off oxygen in the trap one lets the carbon dioxide evaporate and go to another trap kept at minus 80°C and then to the fourth furnace (F_4) which contains copper, copper oxide and silver. The copper oxide and the silver are at both ends of the furnace. The copper is produced by reduction of copper oxide with hydrogen. The copper will reduce nitrogen oxides to nitrogen which can easily be pumped off when the sample is frozen out in the trap to the right of stopcock 11. The sample then goes in the reverse direction and is condensed in the trap between stopcocks 12 and 13.

The gas is then carefully condensed in the next trap. The trap has two walls and in the center a motor-driven stirring rod. At this stage radon is enriched in the gaseous phase and a small amount of gas is pumped away. Carbon dioxide and radon have the vapour pressure 1 atmosphere at -78.5°C and -62°C. The sample is stored in one of the 30 bottles.

The temperatures of the furnaces are

F_1	CuO	about 700°C	F_3		about 350–500°C
	Ag	about 400°C	F_4	Cu	about 450°C
F_2		about 500–400°C		CuO and Ag	about 350°C

The whole chemical apparatus is made of pyrex except some metal manometers and the apparatus for radon separation (copper) and the furnaces (quartz glass or supremax glass).

The chemical system described above has proved not to be quite satisfactory for certain samples (mud). Preliminary experiments with lead chromate in a furnace indicate a definite improvement.

III. *Filling of the counter*

The gas is led through a copper tube and a glass filter to the counter. The pressure is measured relative to the CO_2 pressure in another vessel, the pressure of which is determined with a mercury manometer, 3 m high. The comparison is made with the aid of a small U-shaped mercury manometer.

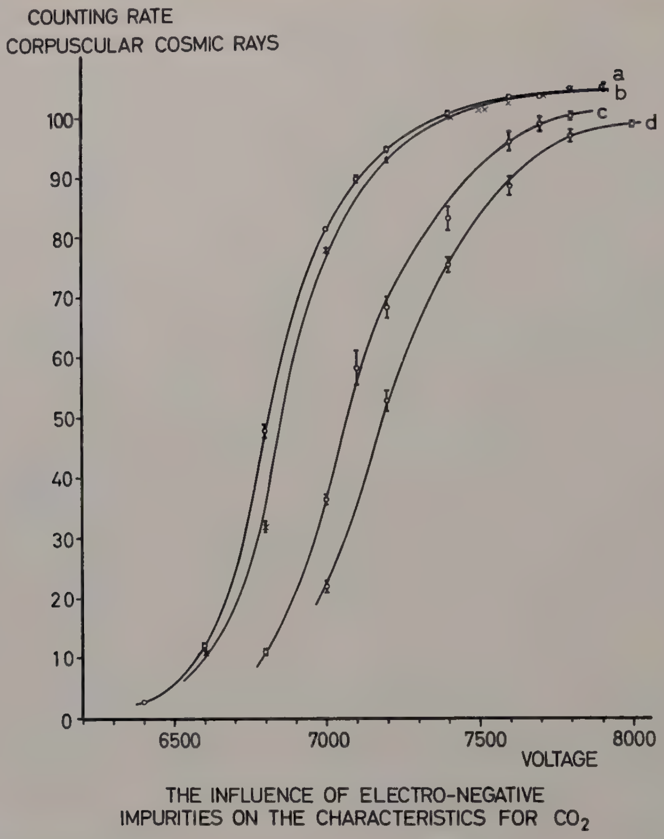

Fig. 9. The displacement of the characteristic of the proportional counter when it is filled with impure samples. The actual amounts of electro-negative impurities have not been measured. All counting rates are expressed in counts/min.

IV. *Dead volume*

When estimating the amount of sample necessary to fill the counter one has to add the volume of the connections and the cooling trap to the real dead volume in the counter itself. In this case this extra volume is as large as 0.2 l since the trap is designed to be large enough even for counter pressures up to 10 atmospheres. We intend to introduce another stopcock and a small trap to reduce this volume.

E. *Calibration samples*

To determine the background we have used anthracite and to determine the effect of modern carbon we have used the cell substance from an elm. We have chosen ten tree rings 160–170 years old.

F. *Determination of the purity of the sample*

Since carbon dioxide is very sensitive to electro-negative impurities, the purity of the gas has to be checked for each sample. For that purpose we use the characteristics of the counter either for the cosmic radiation or a gamma source.

The four curves in Fig. 9 show the displacement and distortion obtained with impure samples. When the carbon dioxide contains an electro-negative gas, the characteristics are displaced towards a higher voltage. This is due to the fact that some of the electrons do not reach the wire but are captured by the impurities. If only a certain fraction, f, reaches the wire, one can compensate for this by chosing a higher voltage. This can only be done for small amounts of impurities when the curves still have a good shape as, for instance, curves a and b in Fig. 9. The higher voltage corresponds to a gas amplification that is higher by a factor $1/f$ than is the case at the normal operating voltage. Instead of changing the operating voltage it is more convenient to apply a correction. Channel 3 may serve to indicate how large the correction must be. Up till now, however, we have checked the purity by counting at a low potential before and after every long period at the normal potential as well as by using channel 3 during the measurements.

G. *Characteristics of the proportional counter*

The curves in Fig. 10 show the counting rate for the two calibration samples. The C^{14} curve shows the net effect of the standard wood sample. Curve a in Fig. 9 gives the net counting rate for the corpuscular cosmic radiation when a higher threshold is used.

H. *Errors in the measurements*

An error of 1% in the net counting rate will give an error of 80 years in the result.

I. *Statistical error*

The curve in Fig. 11 shows the statistical error, expressed in years, for different ages with 48 hours of counting on the standard samples as well as on the unknown sample (with an effect of 8.0 from a modern sample and 1.0 from an infinitely old sample).

II. *Errors in the potential*

The variations in the potential during the measurement are so small that they can hardly be observed. The scale of the meter is divided into 200 volts and is equipped with a mirror and a very thin needle. The error in the potential can be estimated to 20 volts. The displacement of the curves due to impurities is larger for higher potentials. If we apply a correction no higher than 30 volts, then the error must be well below $30/100 \cdot 1\% = 0.3\%$.

III. *Instability in the electronics*

A variation of 5% in the value of the discriminator threshold will give a variation of 5% in the gas amplification, which corresponds to 15 volts in the operating potential [20] and thus 0.15 % in the counting rate.

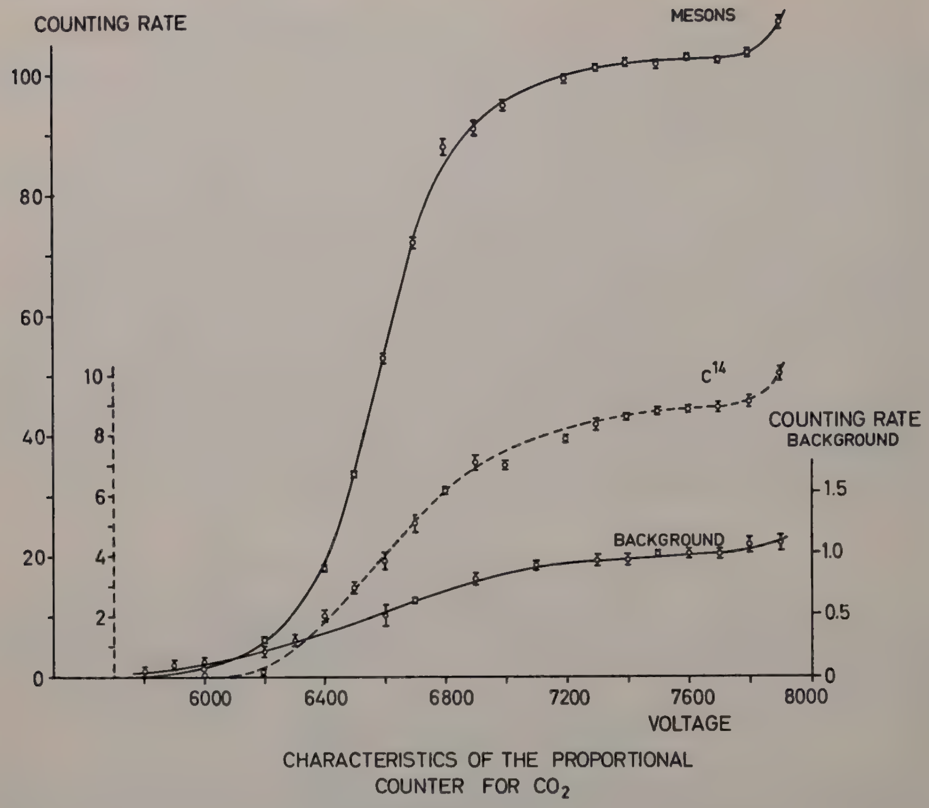

Fig. 10. The characteristics of the proportional counter are not corrected for the barometric pressure. The rates are expressed in counts/min.

The pulses from the anticoincidence counters block the electronic apparatus during

$$1800 \cdot 450 \cdot 10^{-6} \cdot 1/60 \text{ min/min},$$

i.e. during about 1.2 % of the time. An error of 5 % in the pulse length then corresponds to an error in the counting rate of 0.06 %. The observed variations in the Geiger voltage have no influence on the background.

The variations in threshold value and pulse length will be checked as soon as possible.

IV. *Variations in the filling of the counter*

The temperature of the proportional counter is measured with a resistance thermometer. The error is less than 0.2°C corresponding to 0.07 % of the filling pressure. The error in the readings of the manometers is about 1 mm. For three atmospheres the error is thus less than 0.15 %. The shift of the steepest part of the characteristic is 18.0 ± 1.5 volts for a pressure change of 1 cm, according to preliminary measurements made here with the cosmic radiation (see de Vries [20]). A low pressure will

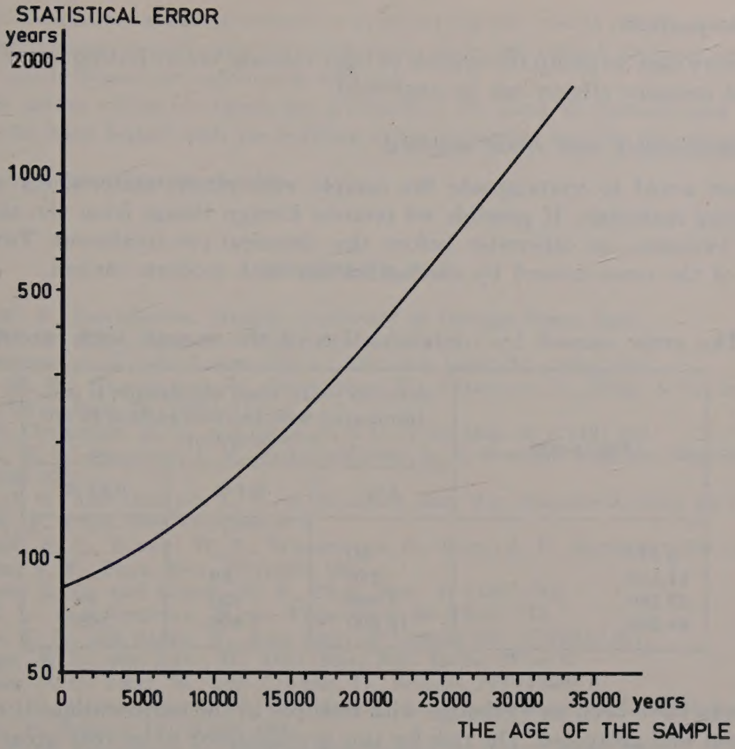

Fig. 11. The statistical error in years as a function of the age of the sample. The error is calculated for 48 hours of counting. The background is 1.0 counts/min. Recent carbon gives 8.0 counts/min.

give a lower counting rate due to the smaller amount of the sample but on the other hand the working potential should be lower than normal.

If the partial pressure of the gases, that are not electro-negative, is kept below 2 mm, the error for 3 atm is less than 0.1%.

V. *Variations in the background*

The background is usually measured once a week. As soon as we have material enough we will examine the variations with barometric pressure. The curve in Fig. 10 is not corrected for the barometric pressure. We have not found any indications of radioactive contamination from other laboratories.

VI. *Radioactive contaminations of the gas*

With channel 4 we have a possibility to determine whether there is any radon in the gas and correct for the radon. As some of the daughter products of radon are beta emitters one has to apply a correction even if one discriminates for alpha radiation.

Krypton (Kr^{85}) is easily pumped away [22] and will not cause trouble in spite of the fact that its boiling point is −153° C.

VII. *Memory effects*

As it is very easy to pump the system to high vacuum before letting a new sample in, the risk of memory effects can be neglected.

VIII. *Contamination with recent material*

One must avoid to contaminate the sample with recent material e.g. paper and impregnating materials. If possible we remove foreign things from the sample with a pair of tweezers, or otherwise before the chemical pre-treatment. Table 5 gives a survey of the error caused by contamination with modern carbon.

Table 5. The error caused by contamination of the sample with recent material.

Age, years	Error in years when the sample is contaminated with modern carbon to an amount of		
	1 %	0.1 %	0.01 %
5 570	80	—	—
11 140	240	20	—
22 280	1 200	120	10
44 560	12 300	1 800	200

There may have been an exchange with isotopes in the surroundings if the sample has not been well protected. The risk for this is considered to be very great especially for bones.

IX. *Isotope separations*

Isotope separation may occur in nature but one can examine the fraction C^{13}/C^{12} and apply a correction. We have an opportunity to get such measurements made in Stockholm.

X. *Errors due to variations in the cosmic radiation*

If the cosmic radiation has varied there may be a systematic error in measurements made with the C^{14}-method, but the error is the same for all stations.

XI. *Errors due to the uncertainty in the half-life of C^{14}*

An error in the half-life of C^{14} will give the same relative error in the ages of the samples.

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